ATMOSPHERIC CHEMISTRY RESEARCH AT THE AIR POLLUTION RESEARCH CENTER, UCR

Roger Atkinson, Janet Arey, Jingsong Zhang and Paul Ziemann

CDAWG

Big Bear, October 20, 2006

Photochemical Air Pollution

- Photochemical air pollution is caused by the interaction of sunlight with oxides of nitrogen ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) emitted into the atmosphere.

Emissions of VOCs and NO_x

- ~1,500 Million tons per year of organic compounds (not including methane) are emitted into the atmosphere from natural (or biogenic) sources and from human activities.
- On a global basis, 80-90% of these non-methane organic emissions are from vegetation.
- NO_x is emitted mainly from combustion sources – vehicles and fossil-fueled power plants being prime examples.

Biogenic VOCs from vegetation

Anthropogenic emissions

Consequences of VOC emissions

In the presence of oxides of nitrogen (NO_x) and sunlight, a series of reactions occur leading to photochemical air pollution, which includes:

- Formation of ozone and other toxic chemicals.
- Formation of secondary aerosol (in addition to directly emitted aerosol).

Morning, vehicle emissions

Afternoon, pollution

50 km altitude

$$O_2 + \text{sunlight} \longrightarrow O + O$$

$$O + O_2 \longrightarrow O_3$$

$$\Big\downarrow \text{ transported downward by convection}$$

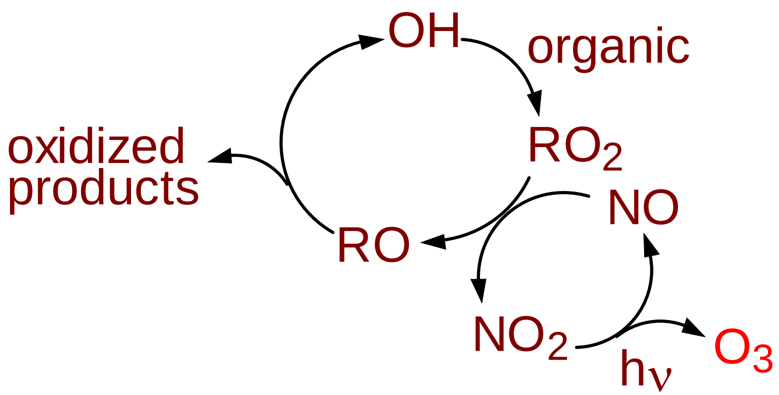
STRATOSPHERE

15 km

$$O_3 + \text{sunlight} \longrightarrow O_2 + O^*$$

$$O^* + H_2O \longrightarrow OH + OH$$

hydroxyl radical



TROPOSPHERE

The hydroxyl (OH) radical is a key reactive intermediate

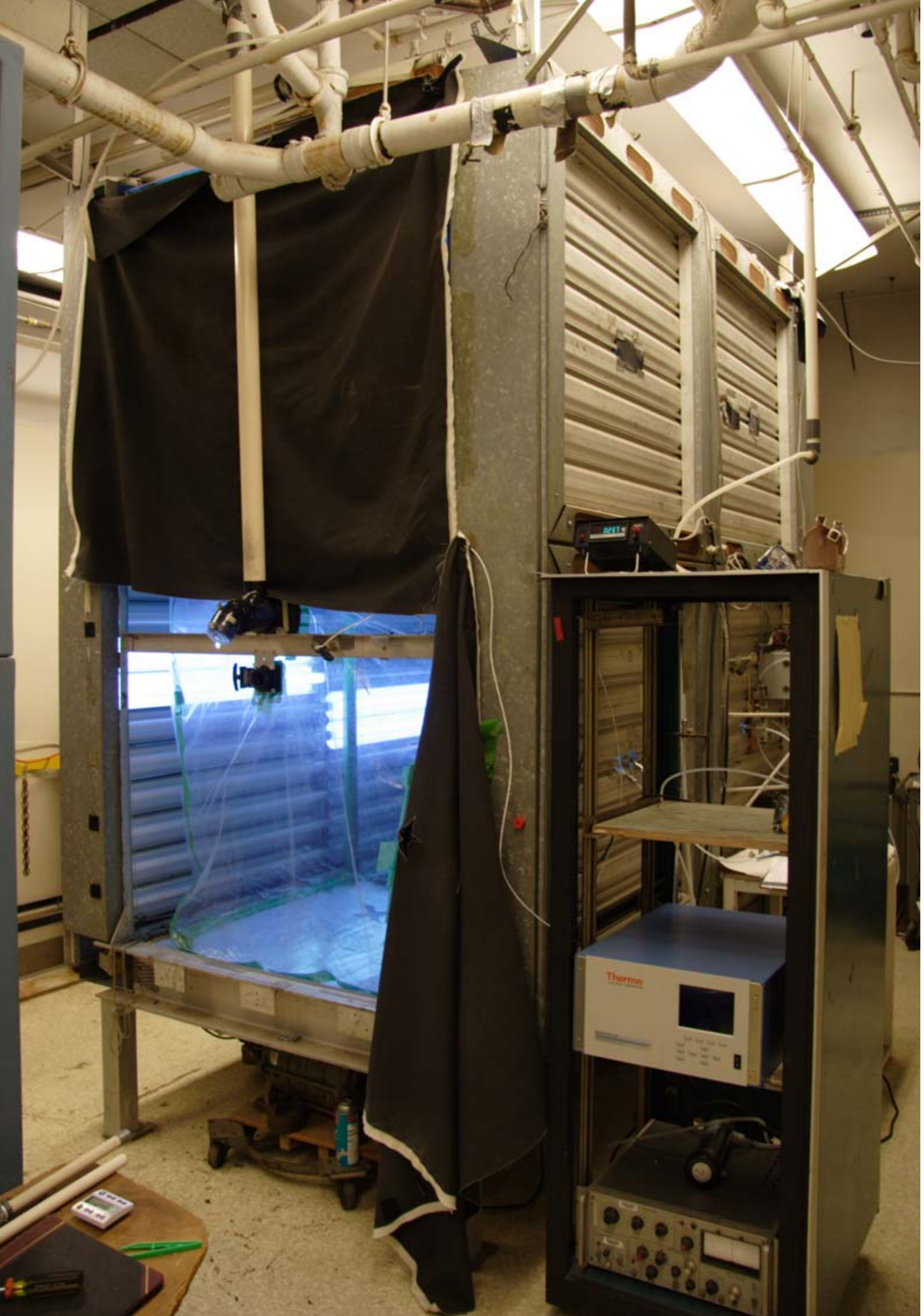
The atmosphere is a large chemical reactor

Current research at APRC

- Kinetics, products and mechanisms of gas-phase reactions of individual VOCs with OH radicals, NO_3 radicals and O_3.
- Chemical pathways leading to formation of secondary organic aerosol from reactions of individual VOCs.
- Ambient measurements of selected organics, including PAHs and nitro-PAHs, and comparison with laboratory studies.
- Real-time ambient measurements of selected chemical species by spectroscopic methods.

Gas-phase studies

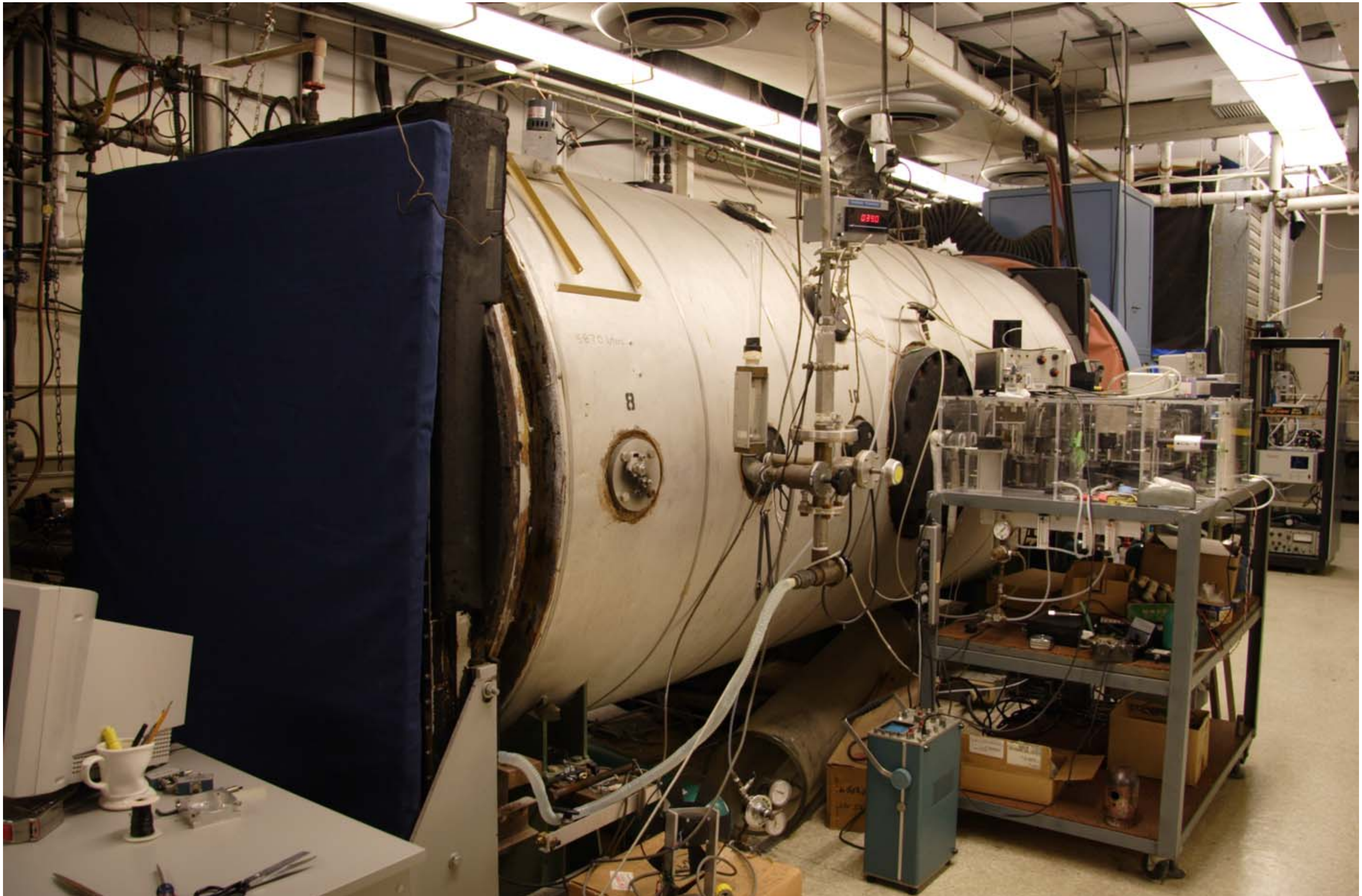
Janet Arey
Roger Atkinson



One of three ~7000 liter volume Teflon chambers.

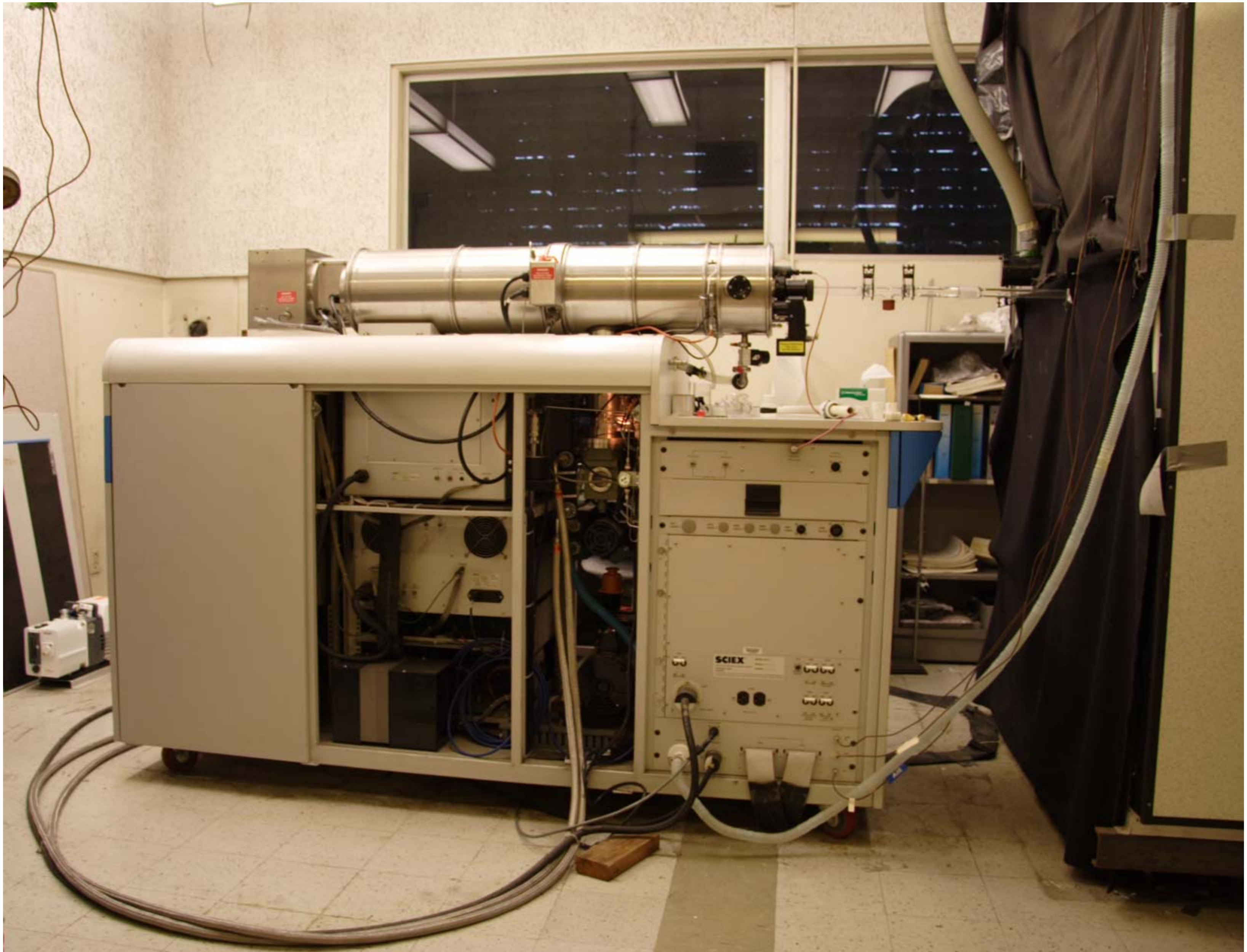
20% of blacklamps are on.

5870 liter volume evacuable chamber



5870 liter volume evacuable chamber

Direct air sampling atmospheric pressure ionization tandem mass spectrometer (API-MS/MS)



Gas and aerosol studies: alkanes

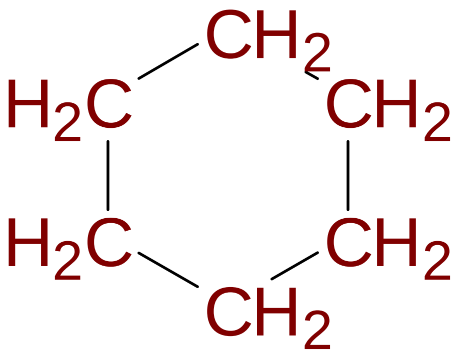
- Liquified petroleum gas (LPG).
- 50-60% of gasoline.
- 50-60% of organics in vehicle exhaust.
- ~50% of non-methane VOCs in air in urban areas.

$CH_3CH_2CH_2CH_3$

n -butane

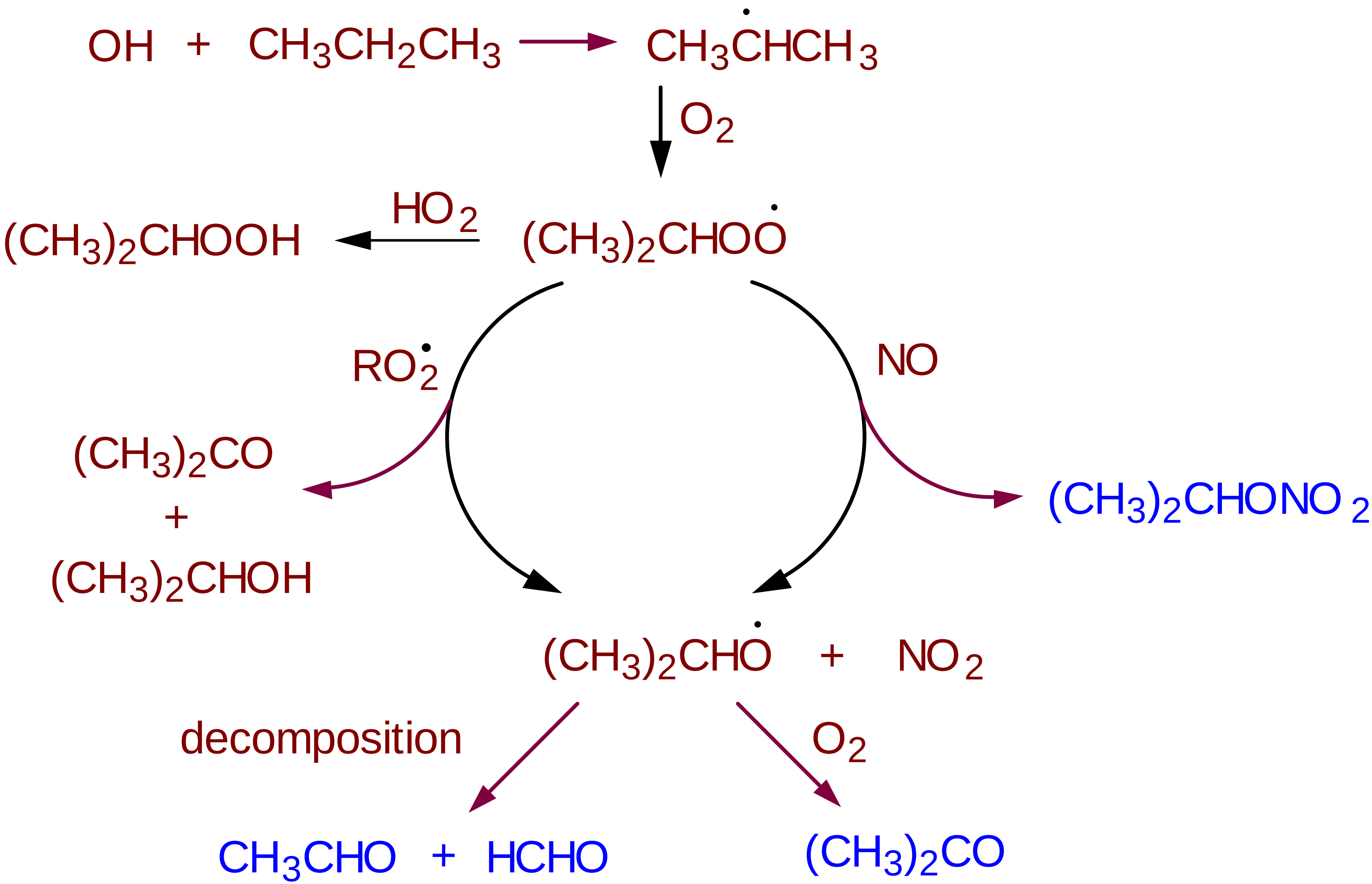
$(CH_3)_3CH$

isobutane



cyclohexane

Alkanes react with OH radicals in the atmosphere

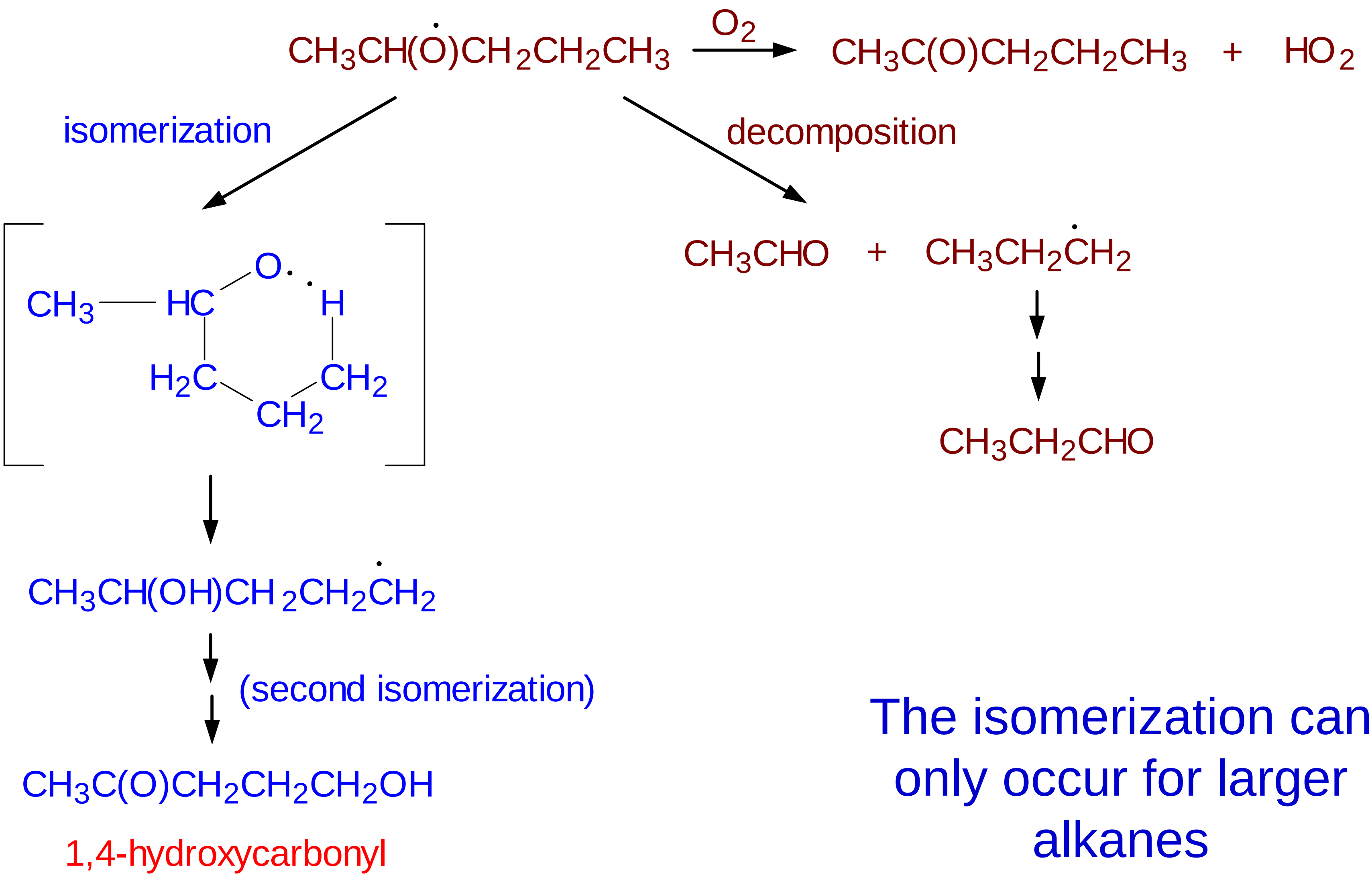


Product yields (as of 1982-1994)

alkane	% carbonyls	% nitrates	% missing
n-butane	84	8	8
n-pentane	~30	12	~58
n-hexane	low	21	high

From data in Carter *et al*., 1976; Atkinson *et al*., 1982.

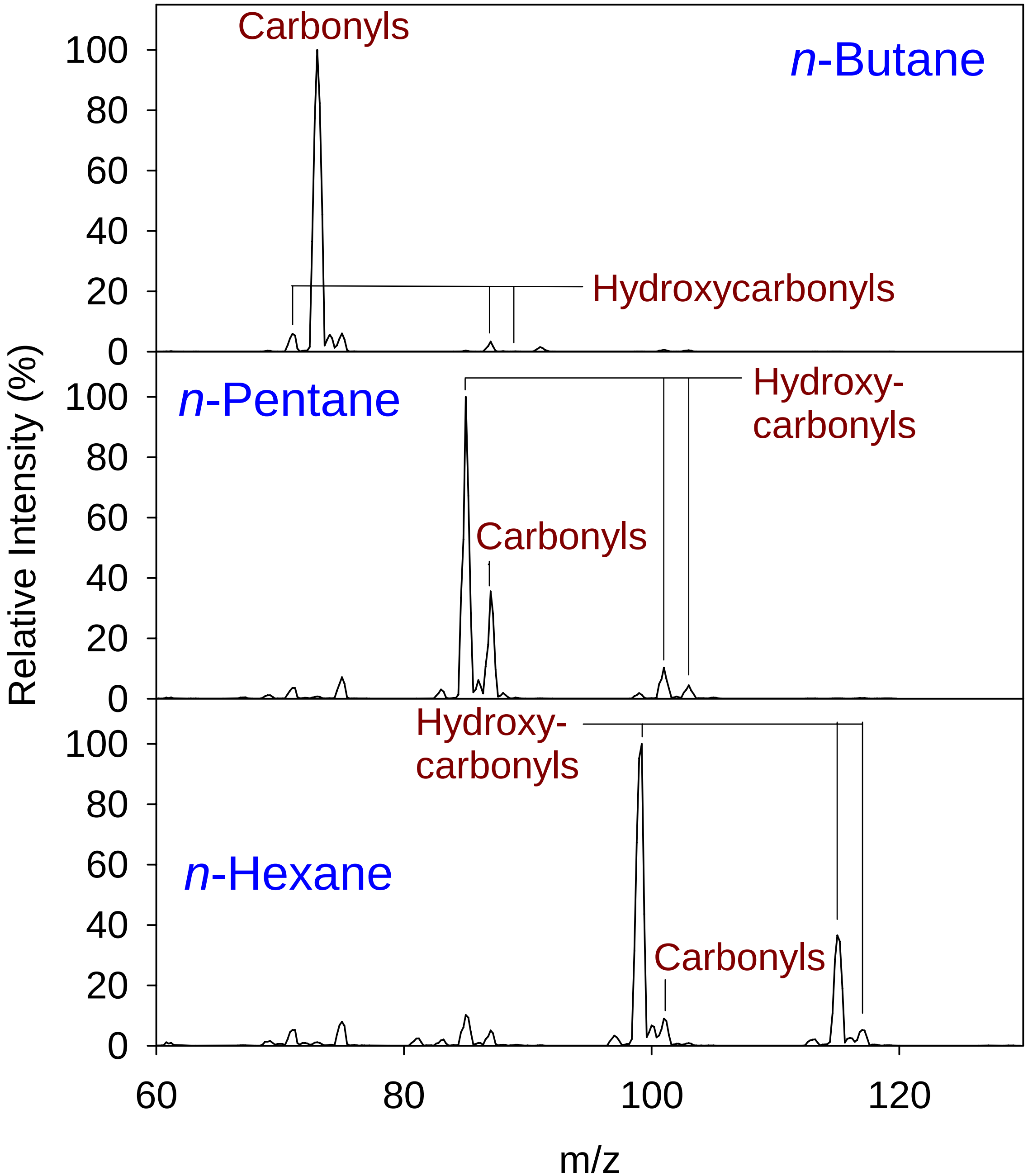
Missing products postulated to be 1,4-hydroxycarbonyls, formed after alkoxy radical isomerization (Carter *et al.*, 1976)



The isomerization can only occur for larger alkanes

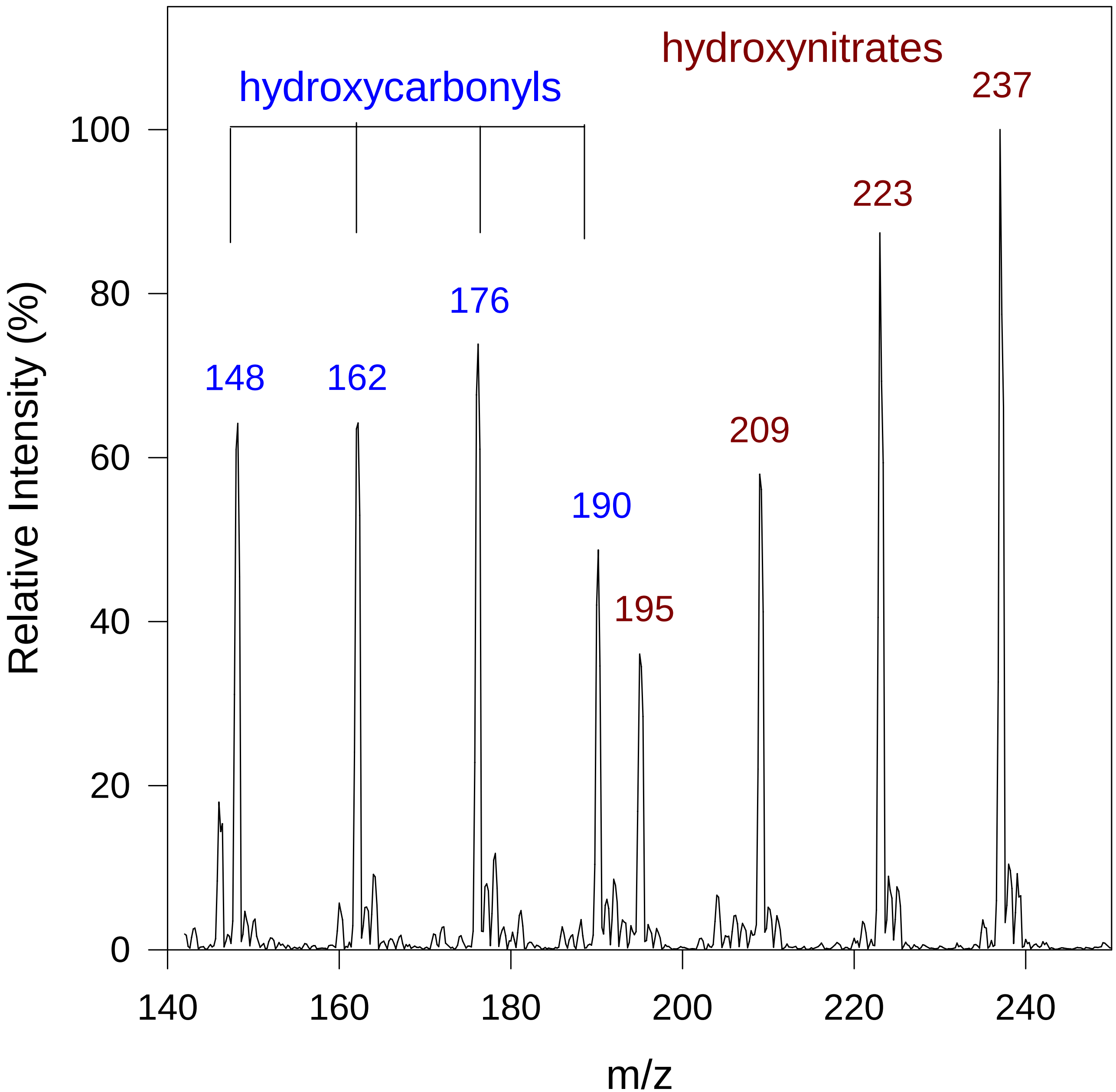
Further progress was halted until new analytical techniques became available

API-MS analyses in positive ion mode



API-MS spectra of OH + *n*-butane, *n*-pentane and *n*-hexane

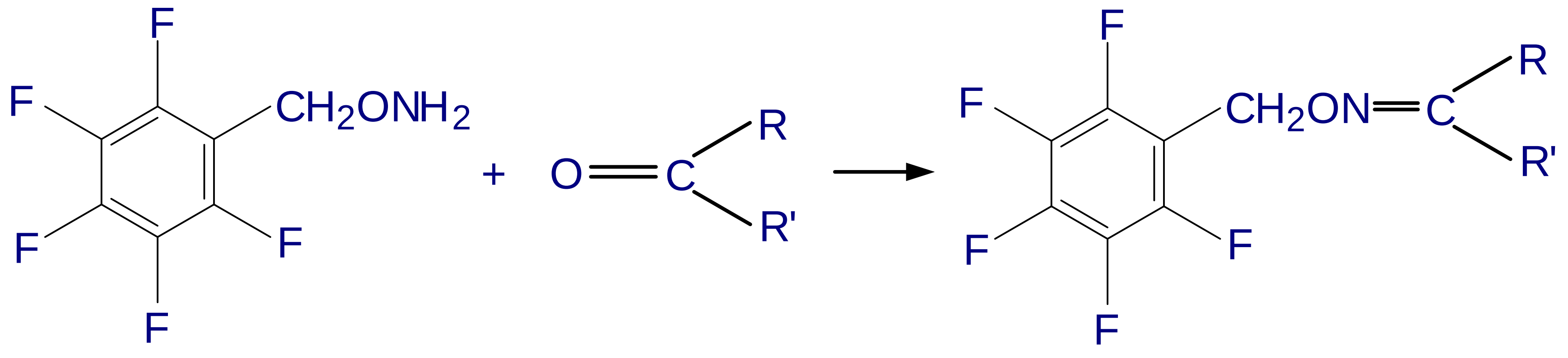
API-MS analyses in negative ion mode



OH + C_5-C_8 *n*-alkanes: NO_2^- adducts

Solid-Phase MicroExtraction fibers

Can be coated with a chemical for on-fiber derivatization of carbonyl-containing compounds, followed by GC analyses.

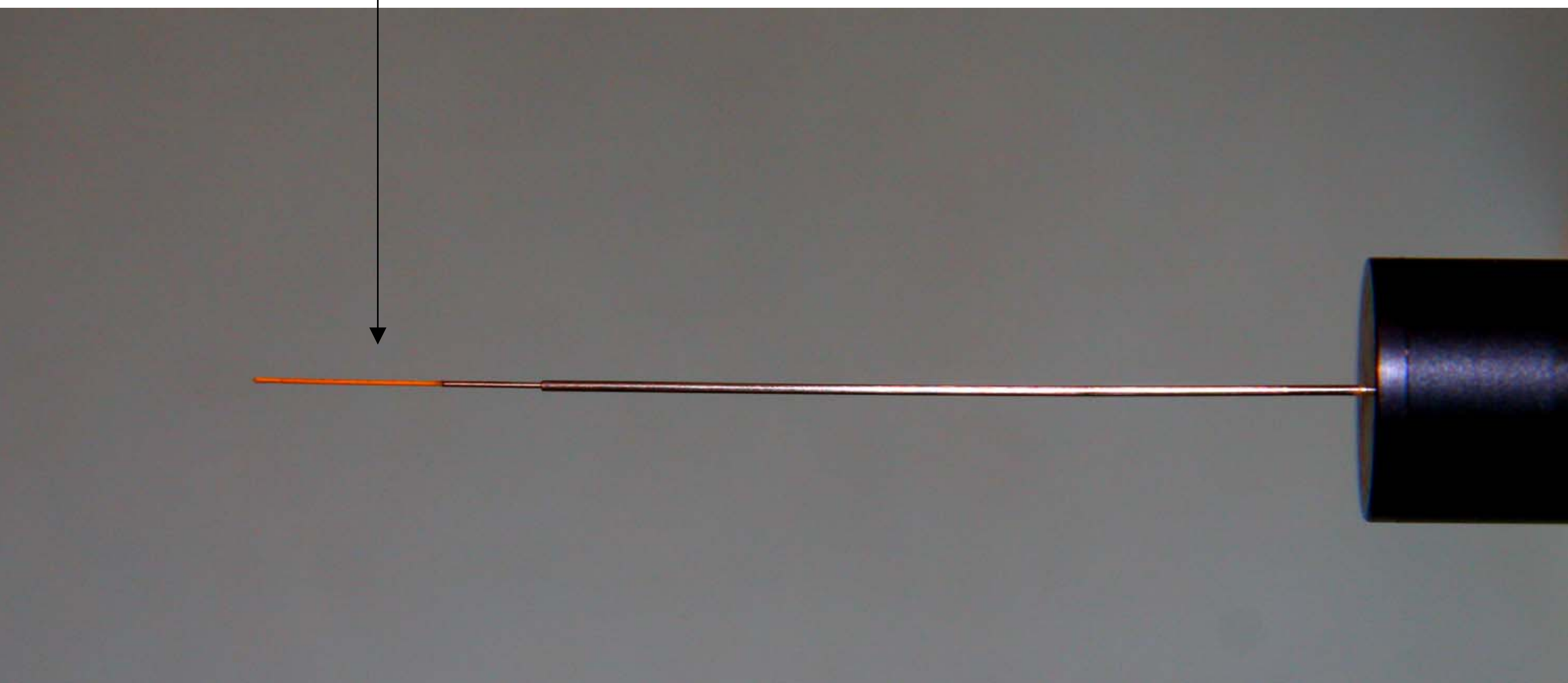


PFBHA

oxime

Fibers are retractable. After coating with PFBHA, the fibers are exposed to the chamber contents with the chamber mixing fan on for typically 5 min.

Fiber, ~20 mm long



Product yields (%) in air at 50% RH

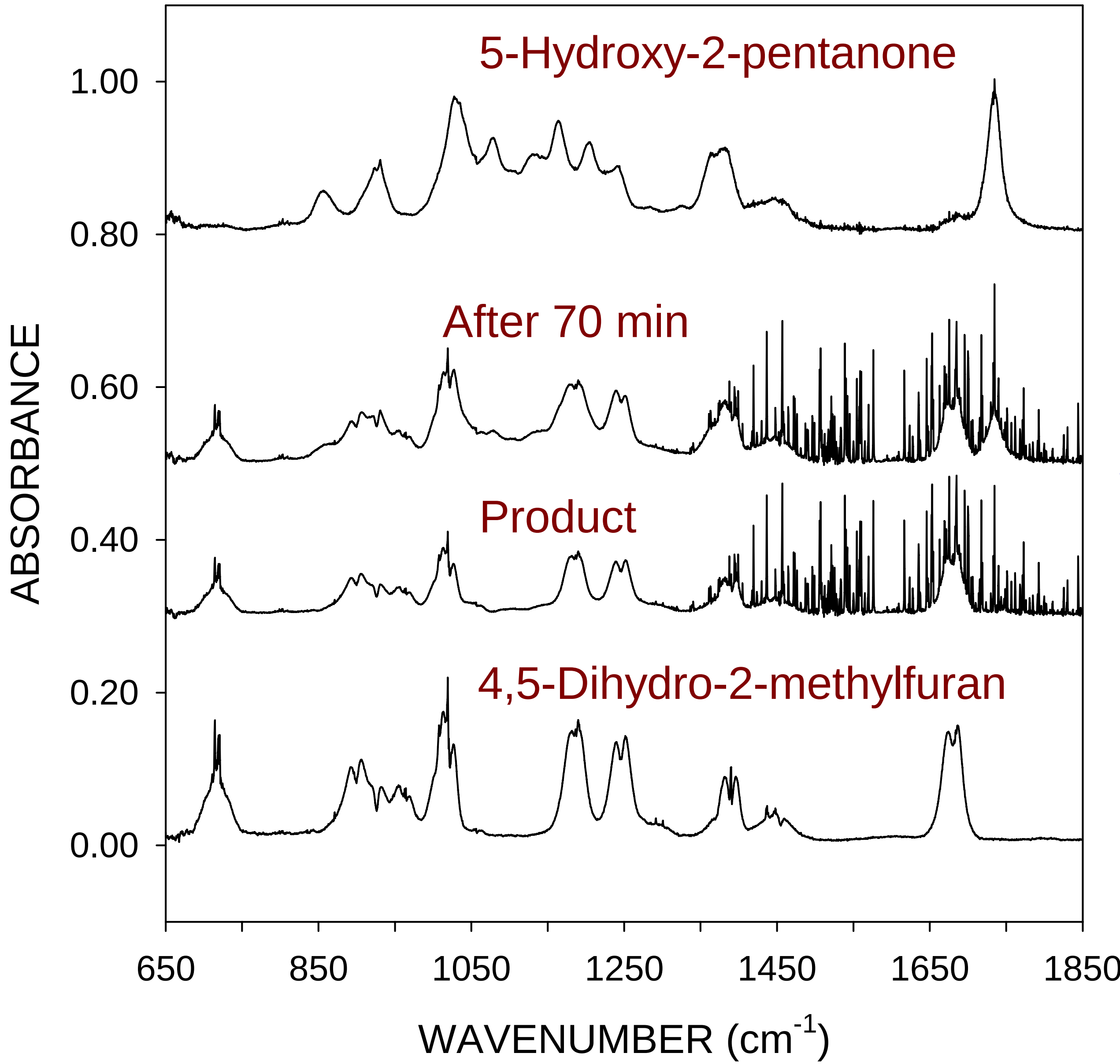
alkane	carbonyls	nitrates	hydroxy-carbonyls	hydroxy-nitrates
n-pentane	50	10.5	54 (36)	2.6
n-hexane	10	14	57 (53)	4.6
n-heptane	<1	18	51 (46)	4.7
n-octane	<1	23	53 (27)	5.4

Yields in parentheses from API-MS in dry air (3-5% RH)

Success so far!

But what happens to 1,4-hydroxycarbonyls in the atmosphere?

5-Hydroxy-2-pentanone (5H2PO) is the only commercially available 1,4-hydroxycarbonyl

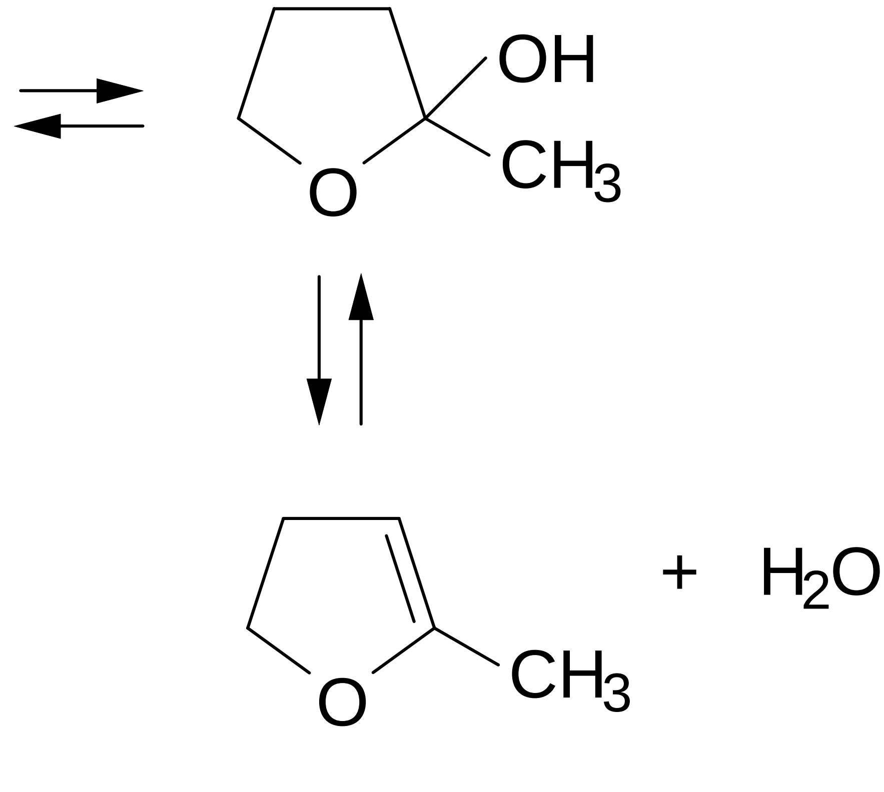


FT-IR spectra of a 5H2PO - N_2 mixture in the dark

5-Hydroxy-2-pentanone has lifetime of 1.1 hr in dry air.

4,5Dihydro-2-methylfuran is stable in dry air, but converts to 5H2PO at 5% relative humidity, with a lifetime of 3.5 hr.

$CH_3C(O)CH_2CH_2CH_2OH$



5-hydroxy-2-pentanone

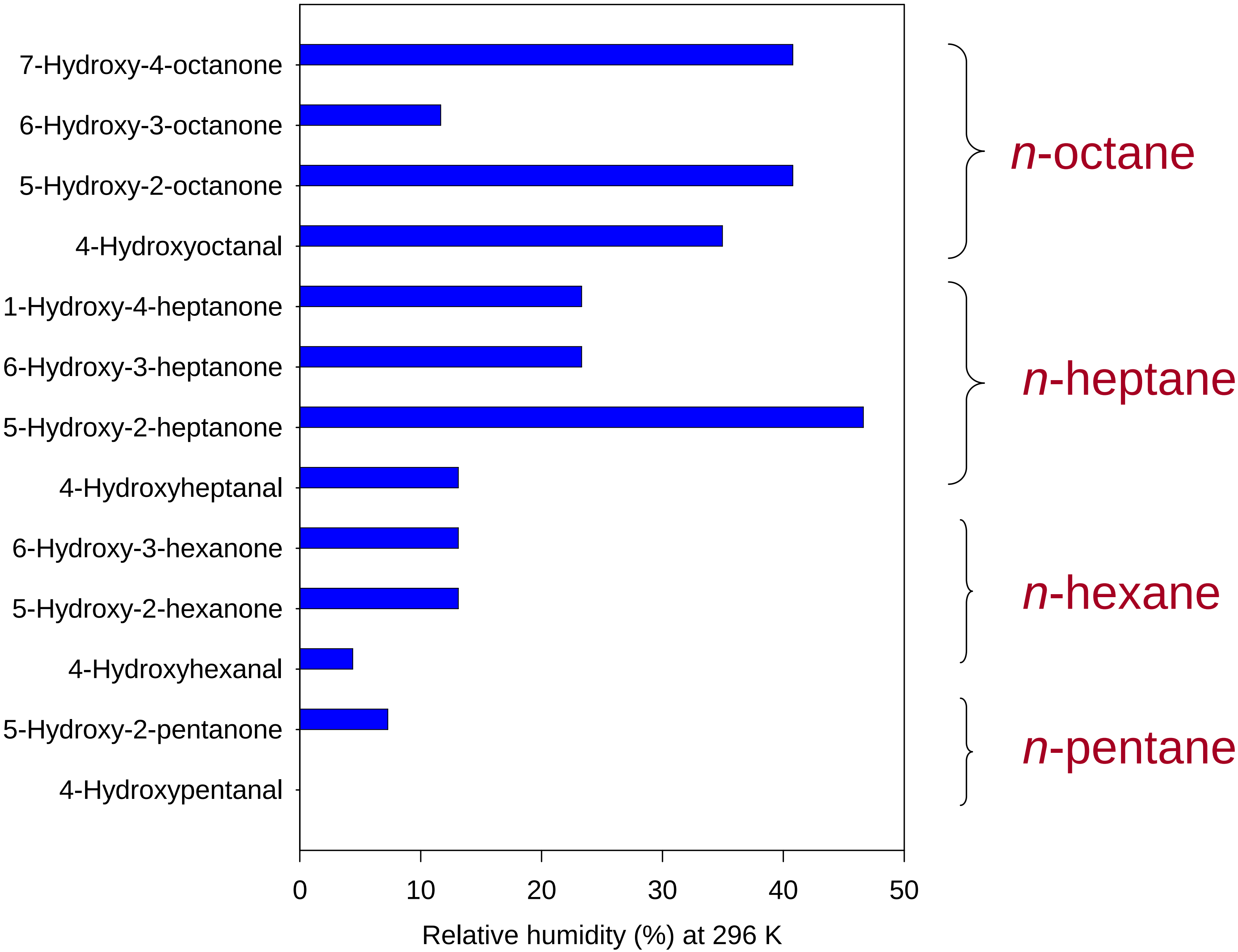
4,5-dihydro-2-methylfuran

Reactions of 5-hydroxy-2-pentanone and 4,5-dihydro-2-methylfuran

- 4,5DH2MF reacts very rapidly with OH radicals, NO_3 radicals, and O_3. Daytime lifetimes:

n-Pentane:	1.5 day	(OH)
5-Hydroxy-2-pentanone:	9 hr	(OH)
4,5-Dihydro-2-methylfuran:	38 min	(OH)
	7 min	(O_3)

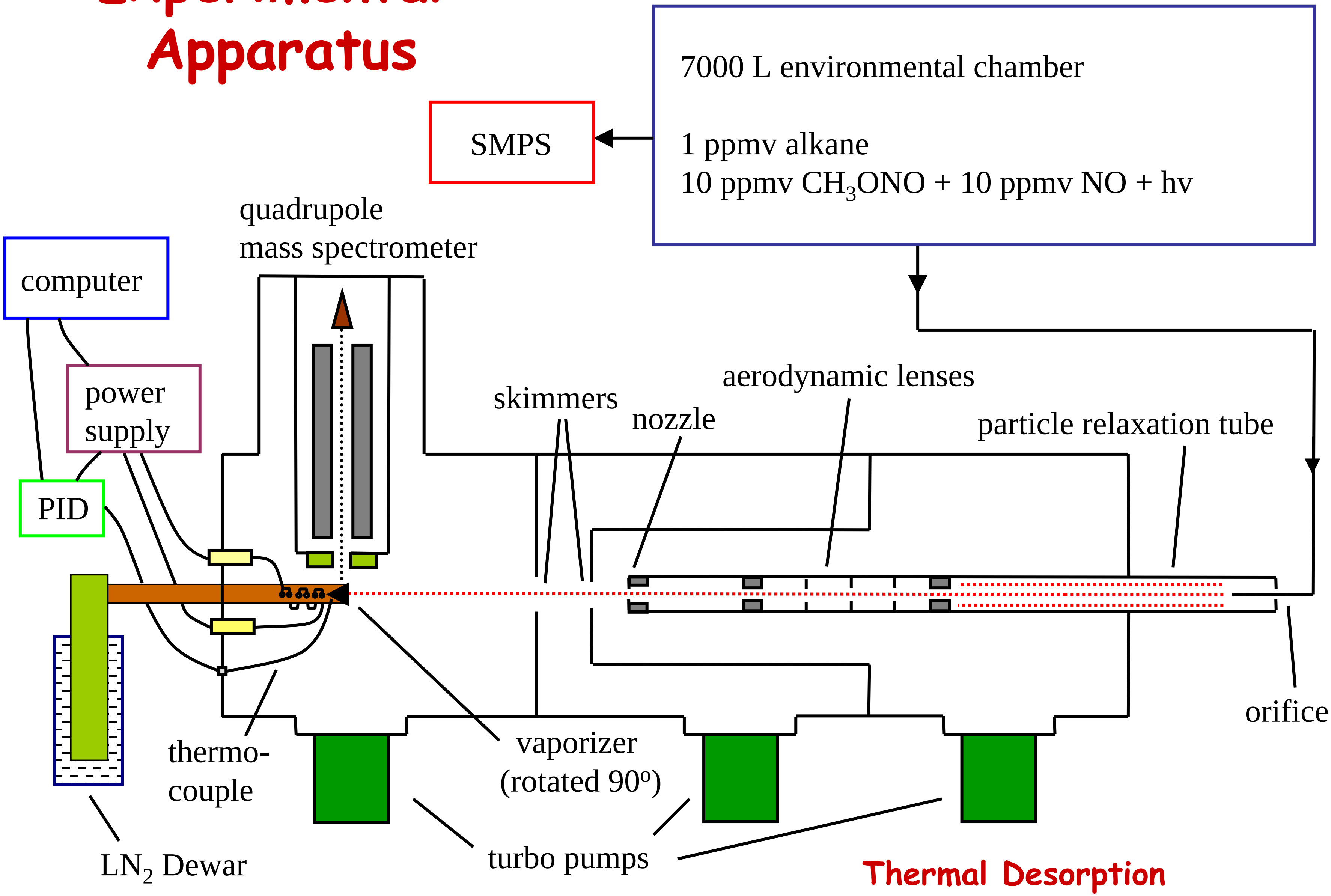
Relative humidities where dihydrofuran formation is important



Aerosol-phase studies

Paul Ziemann

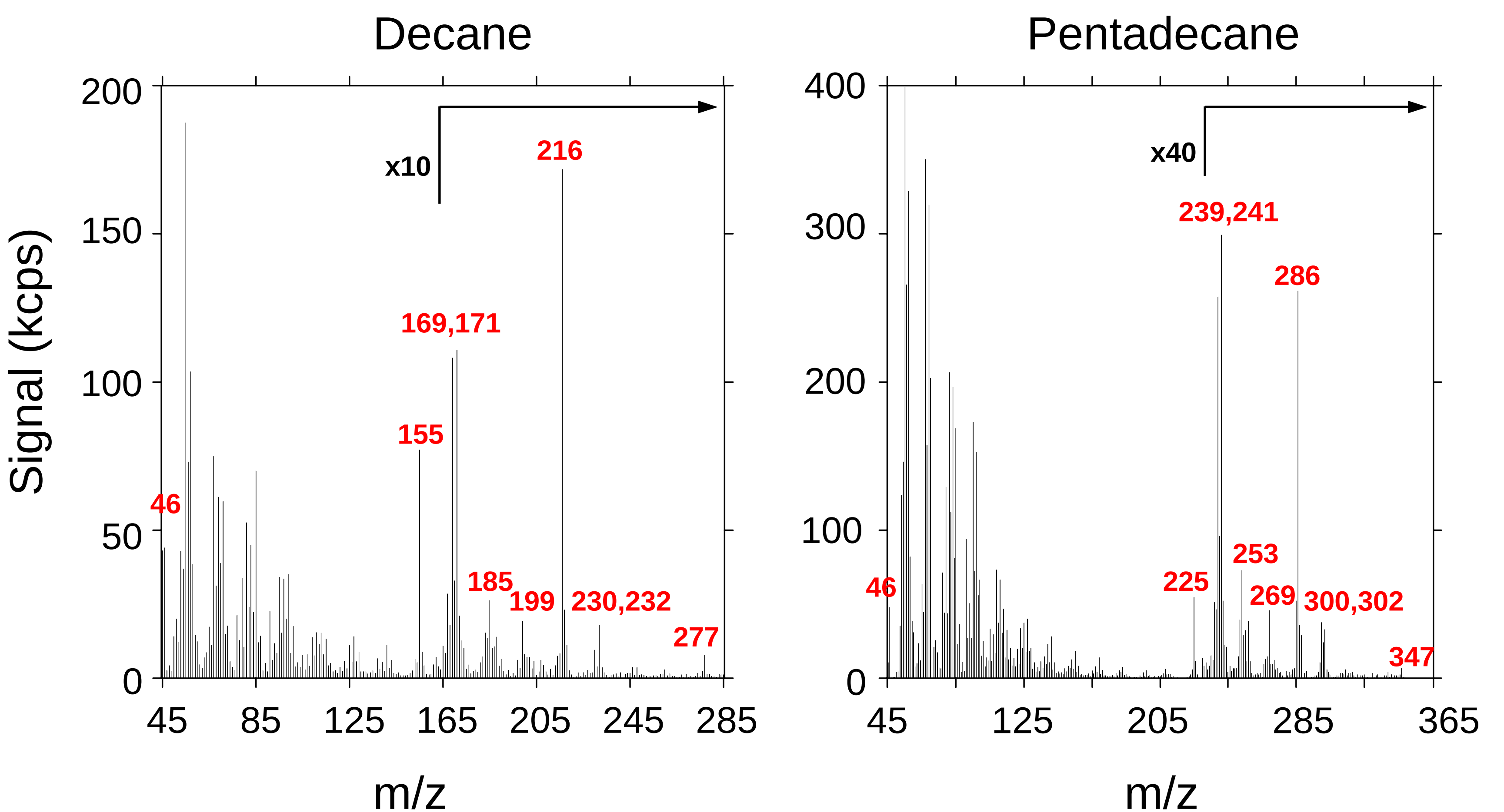
Experimental Apparatus



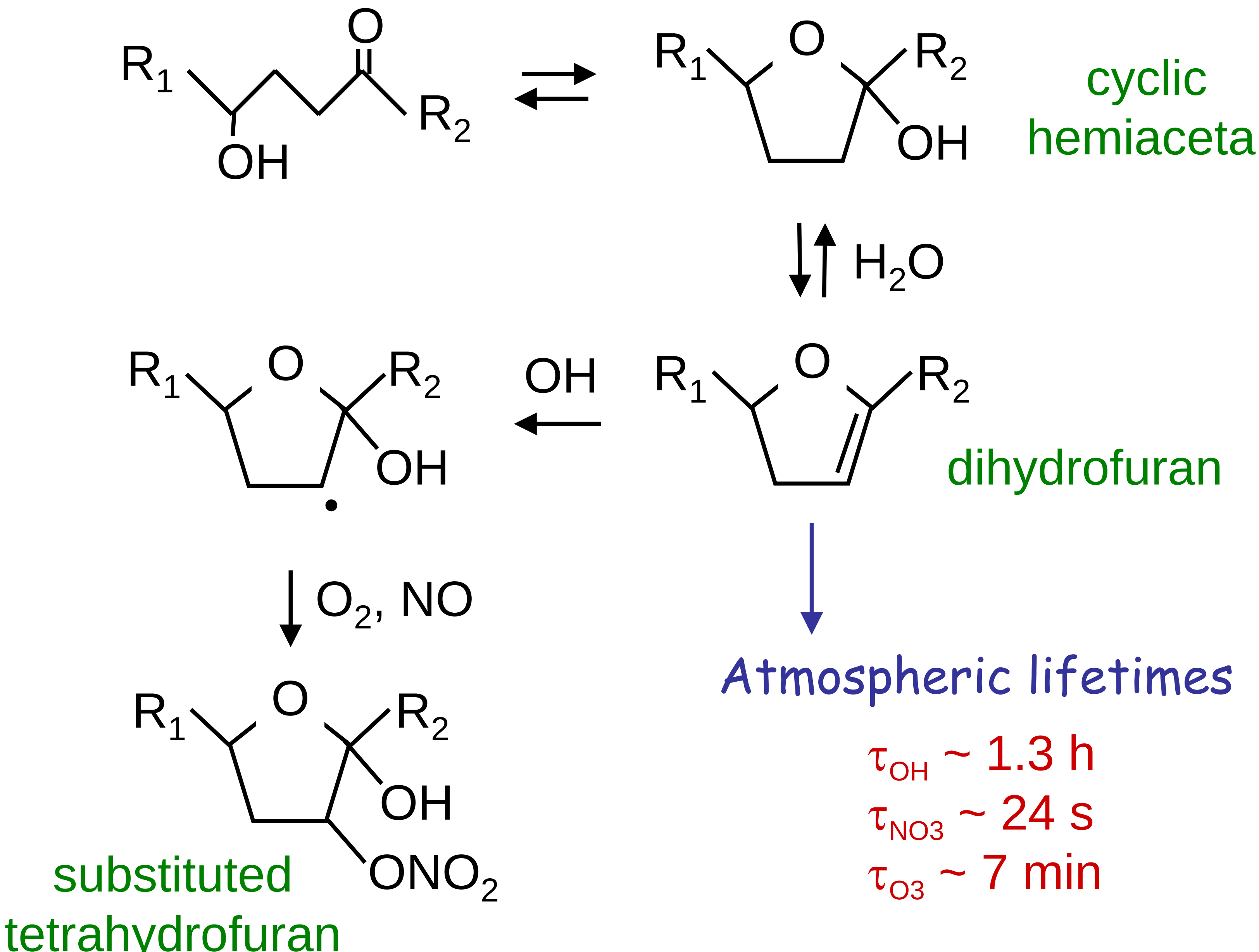
Thermal Desorption

Particle Beam Mass Spectrometer (TDPBMS)

Real-Time Mass Spectra of SOA from Decane and Pentadecane + OH/NO_x



Reactions of 1,4-Hydroxycarbonyls



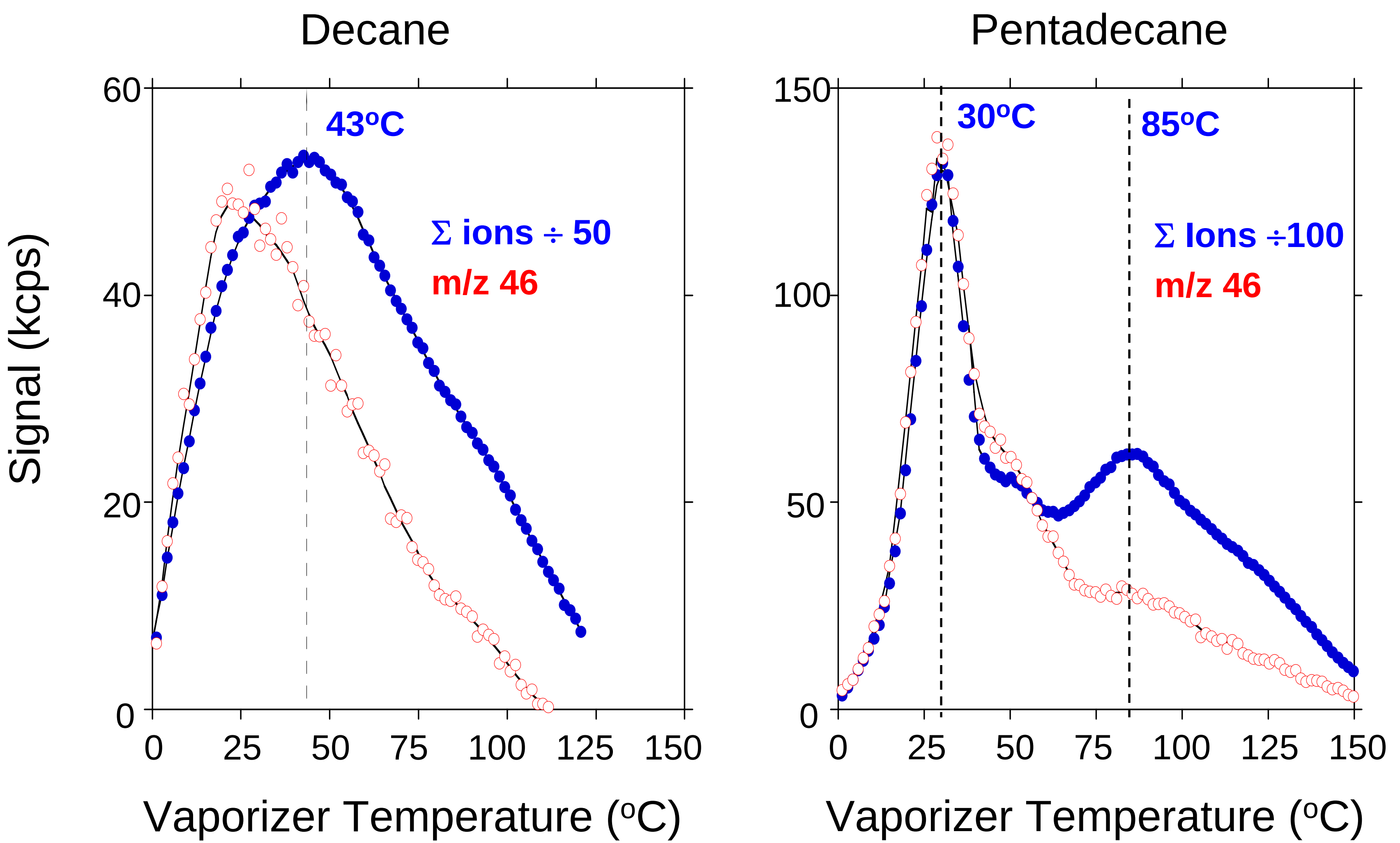
Atmospheric lifetimes

$\tau_{OH} \sim 1.3$ h

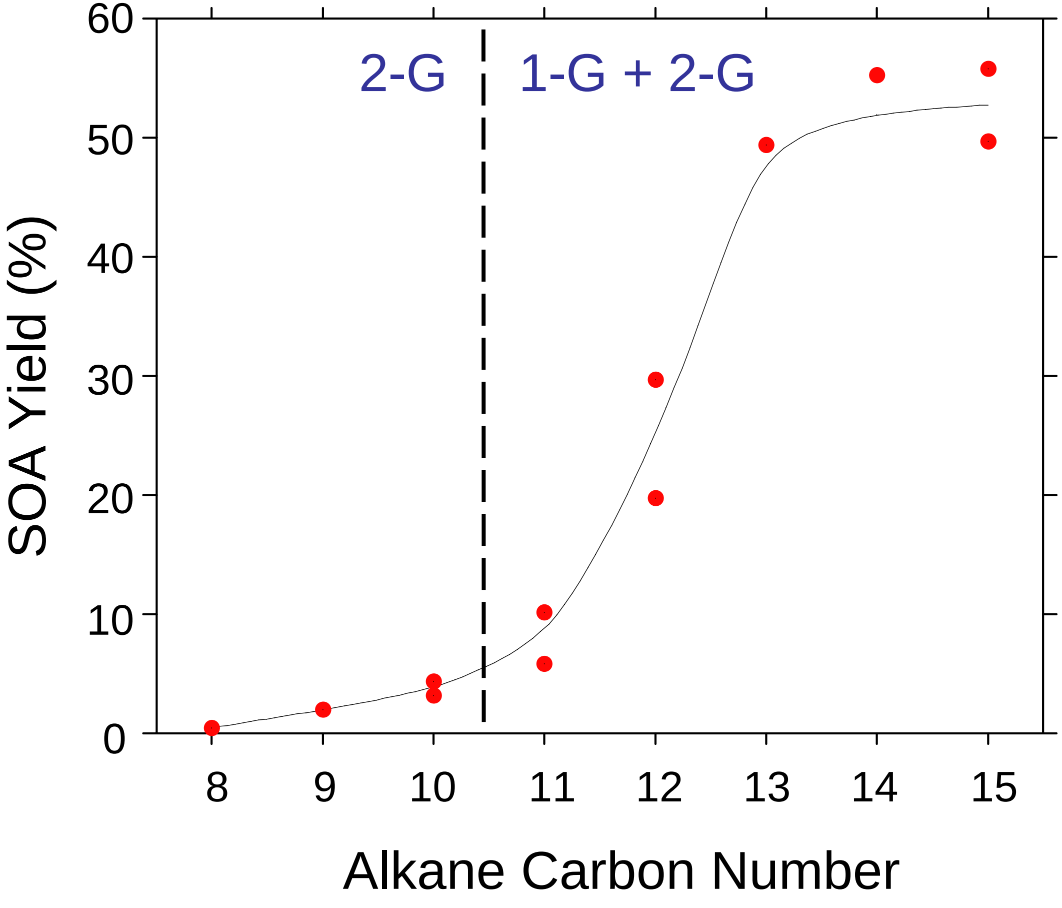
$\tau_{NO3} \sim 24$ s

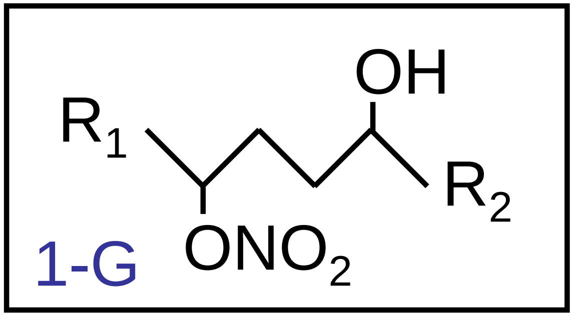
$\tau_{O3} \sim 7$ min

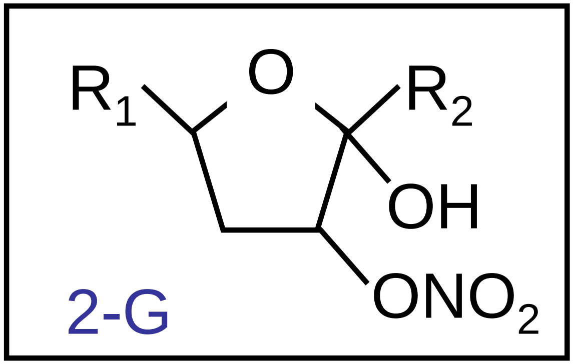
Desorption Profiles of SOA from Decane and Pentadecane + OH/NO_x



SOA Yields from Linear Alkanes + OH/NO_x



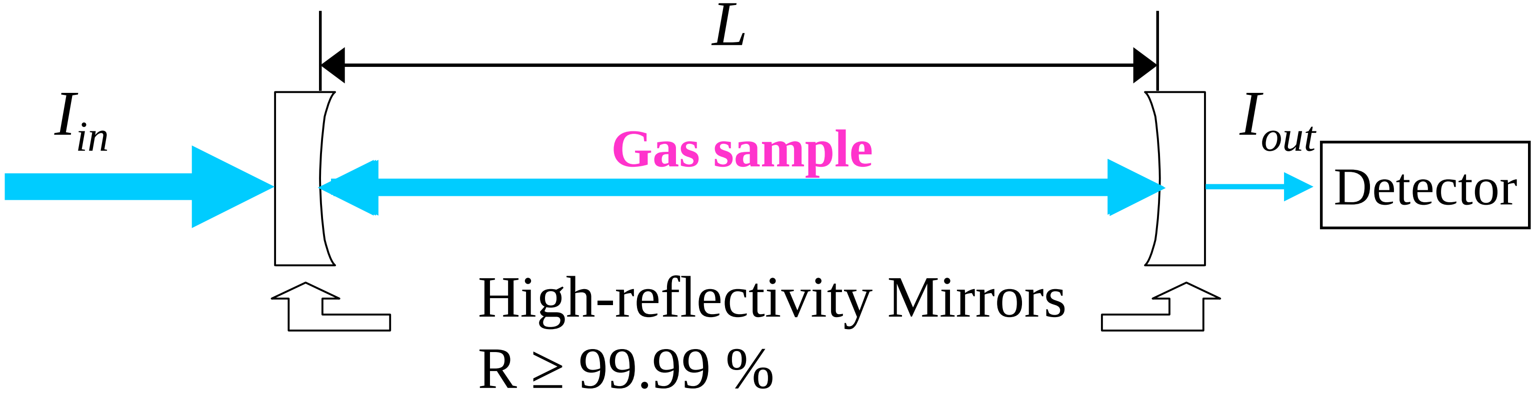




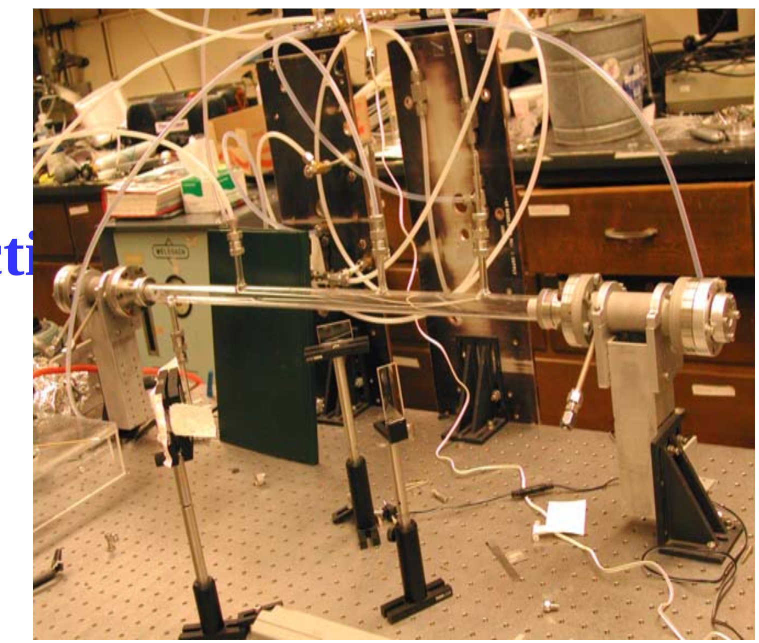
Zingsong Zhang

Spectroscopic studies

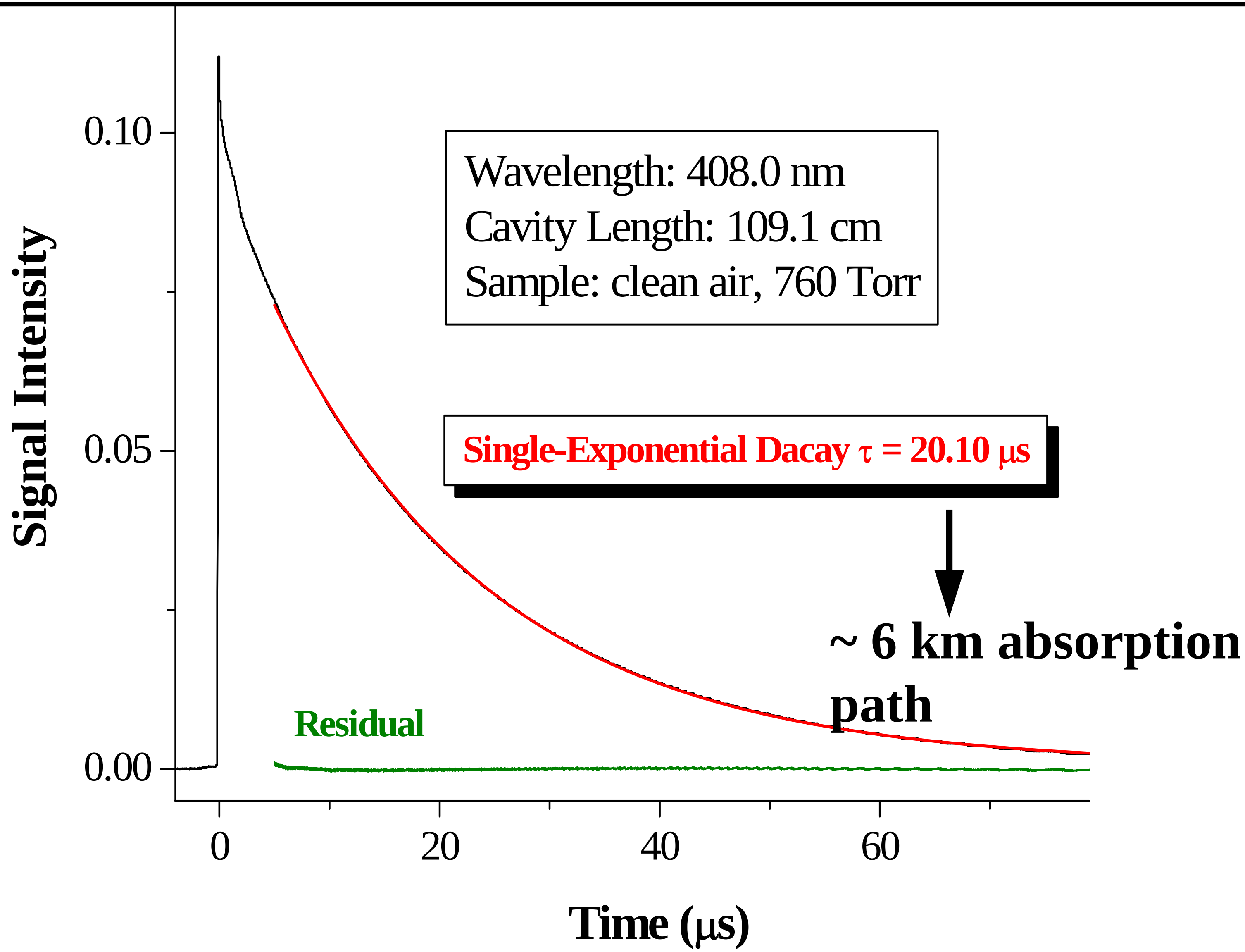
Cavity Ring-Down Spectroscopy (CRDS)



- **Quantitative and absolute measurements**
- **High sensitivity with a long effecti absorption path (~ km) in a compact setup (~ m)**
- **Spectroscopic selectivity**
- **Real-time and in-situ detection**



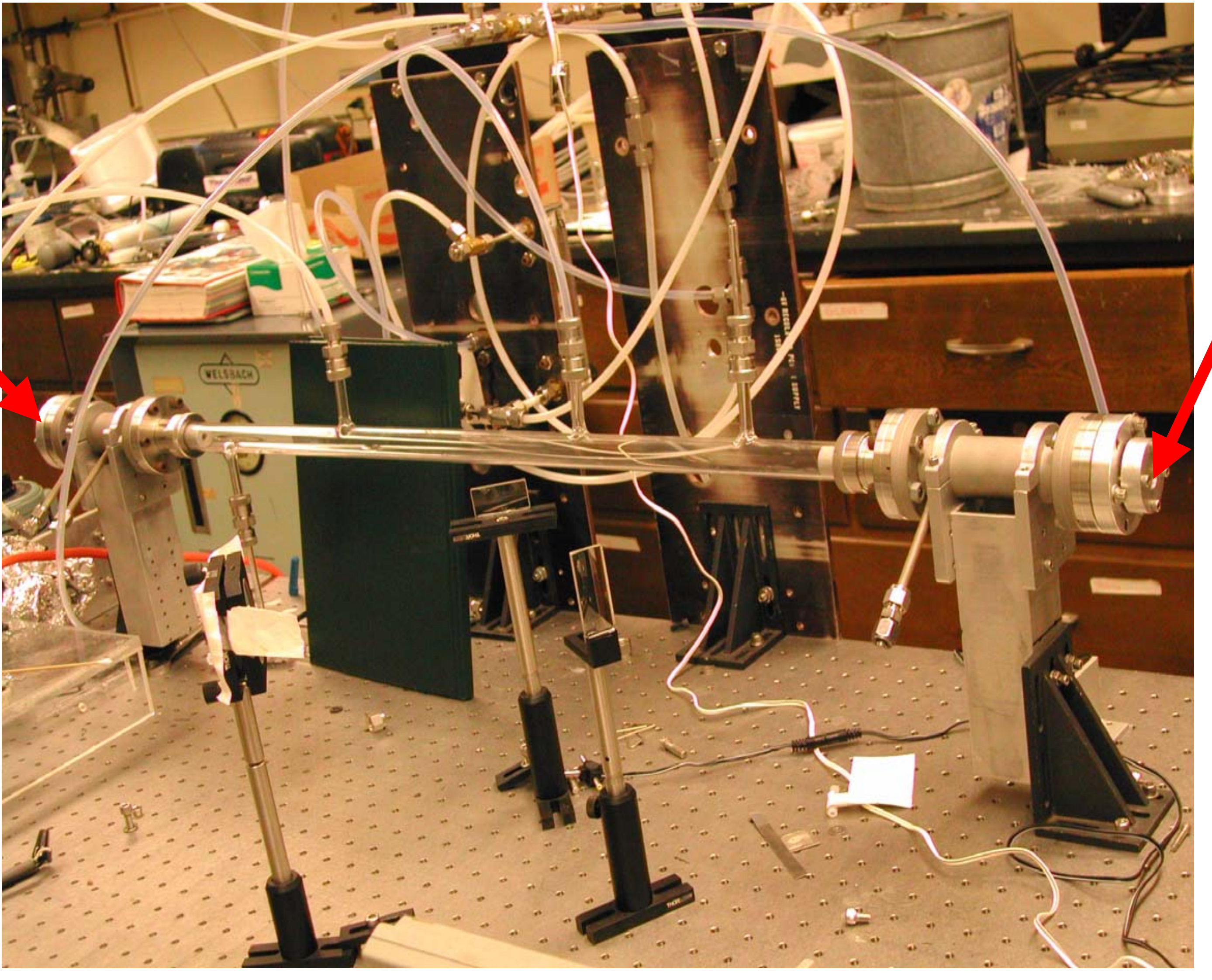
Typical CRDS Signal



Usable data in ~ 3.5 τ, effective absorption length ~ 21 km (Speed of light = 300 m/μs**)**

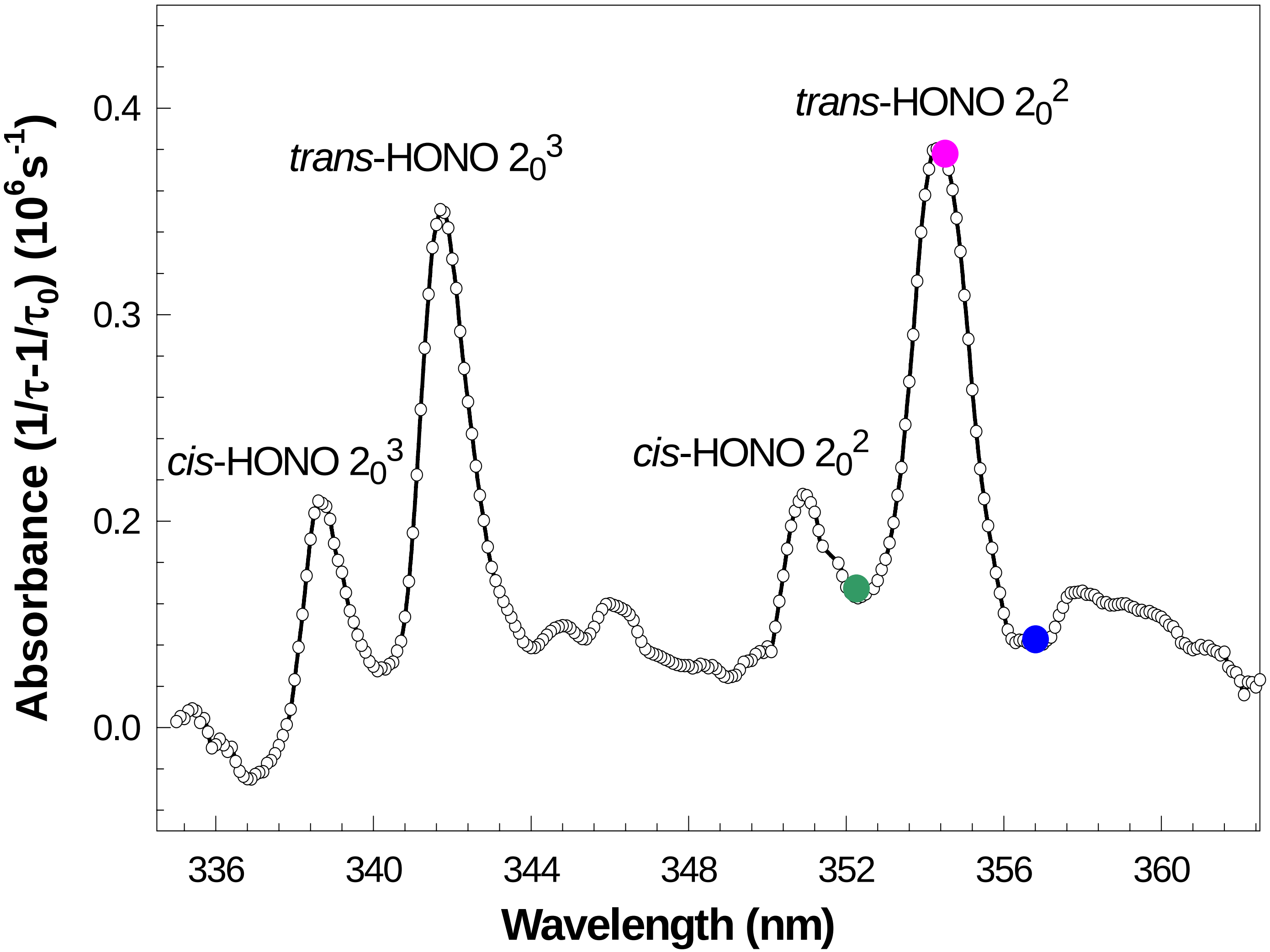
Cavity Ringdown Spectrometer

Mirror



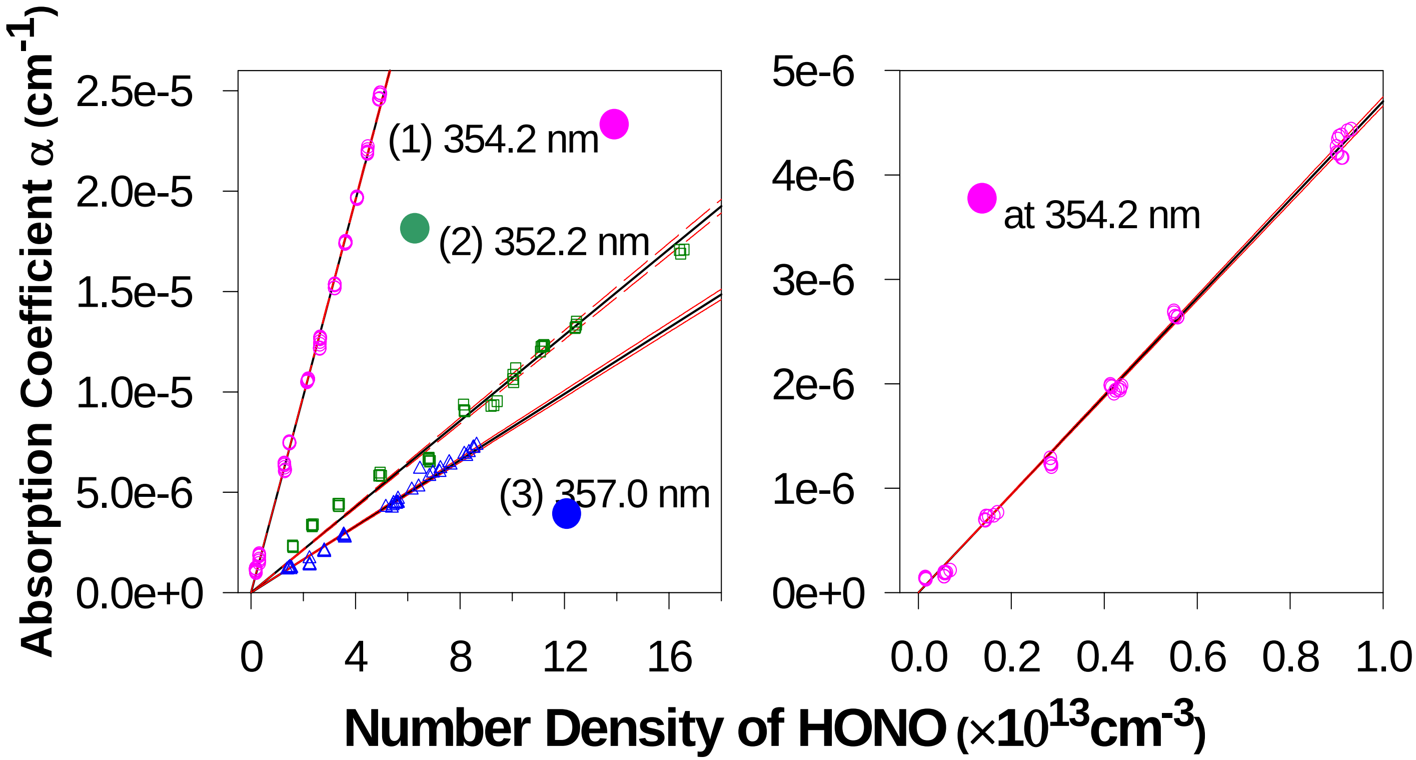
Mirror

CRDS Absorption Spectrum of HONO



HONO Concentration ~ 1 ppm

CRDS Detection of HONO

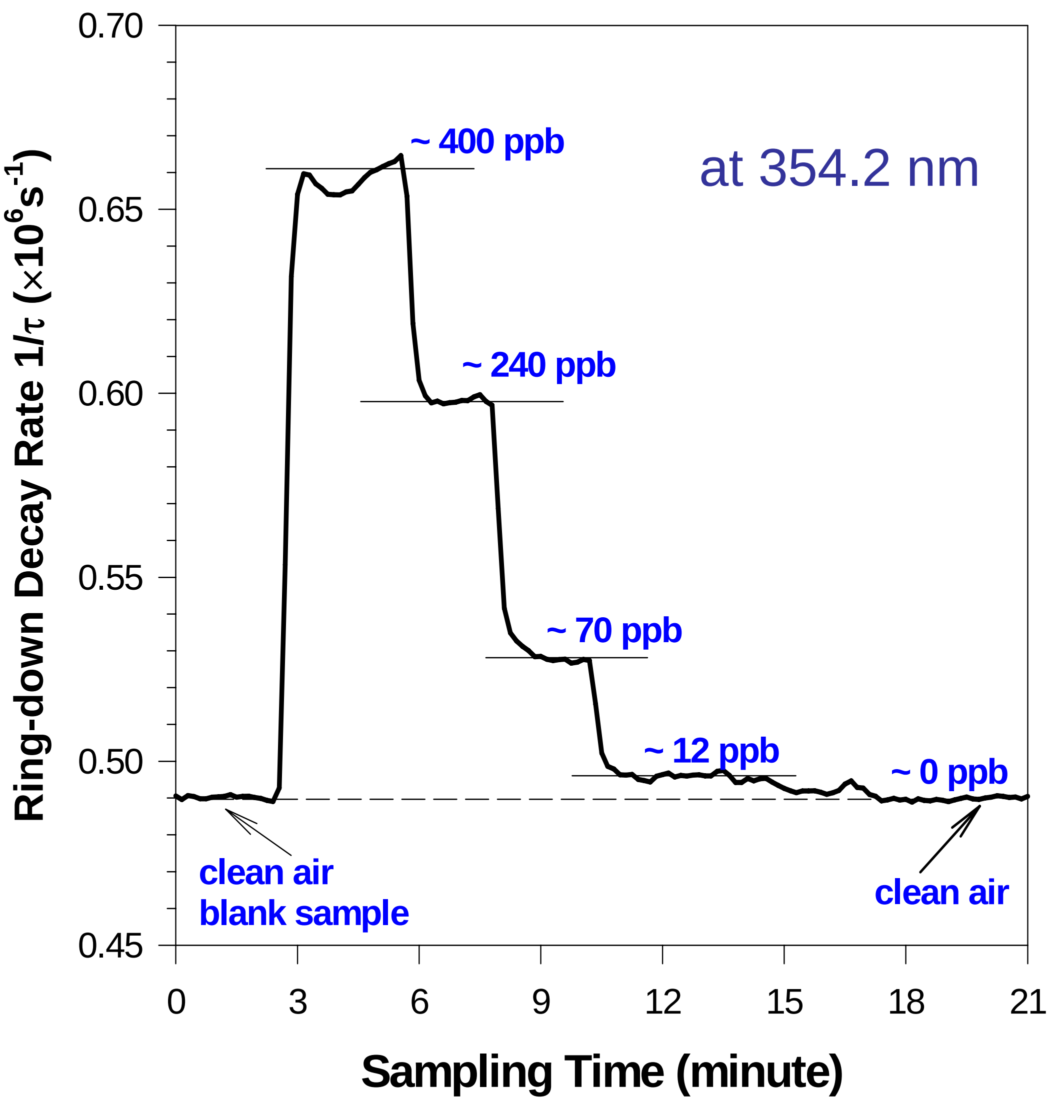


Linear response
Large dynamic range
High detection sensitivity

Number density of HONO is based on measurements using a NO-NO_x Analyzer

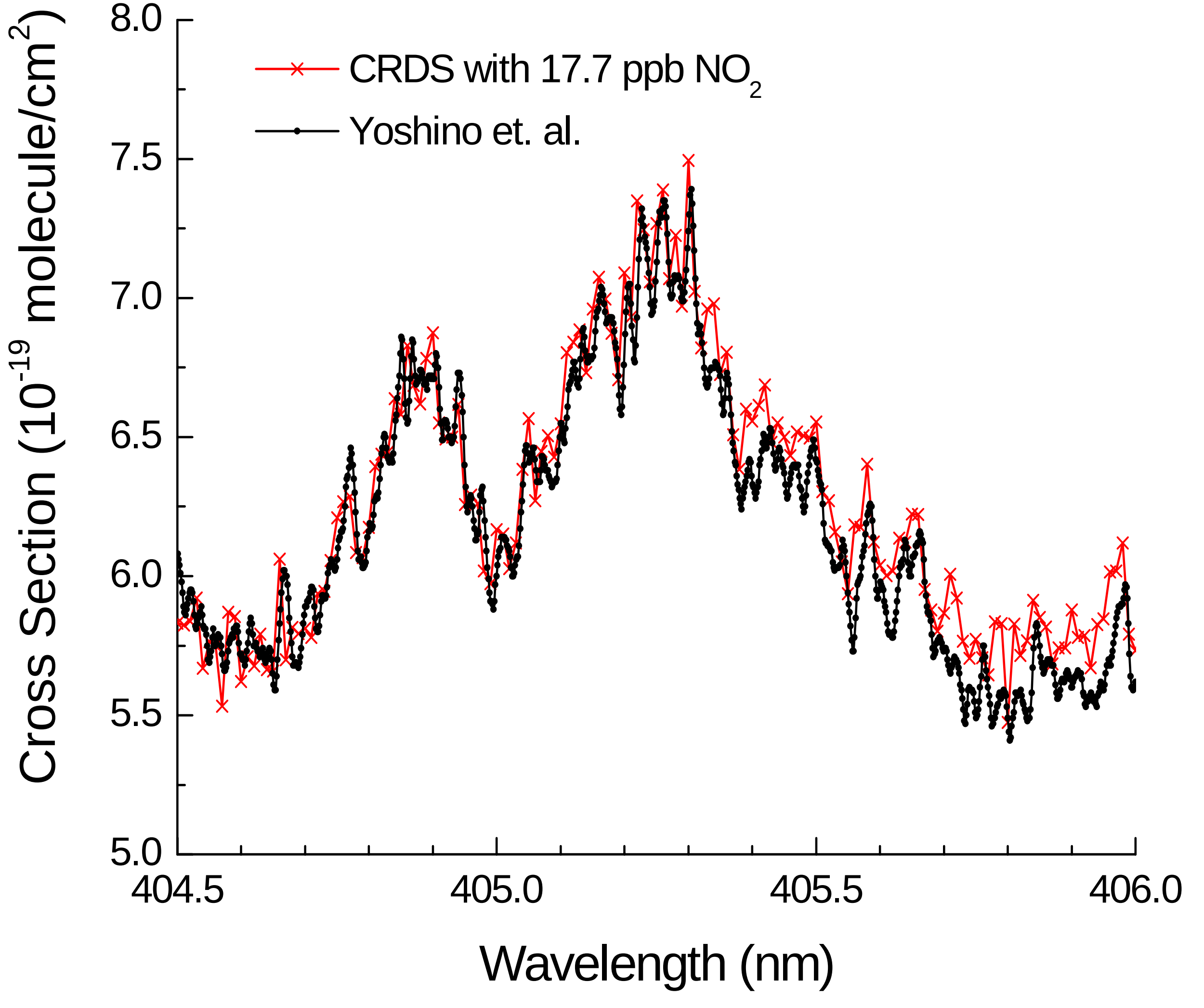
1 ppm = 2.38×10^{13} molecules/cm^3 at 735 Torr and 25^{o}C

Detection Sensitivity for HONO

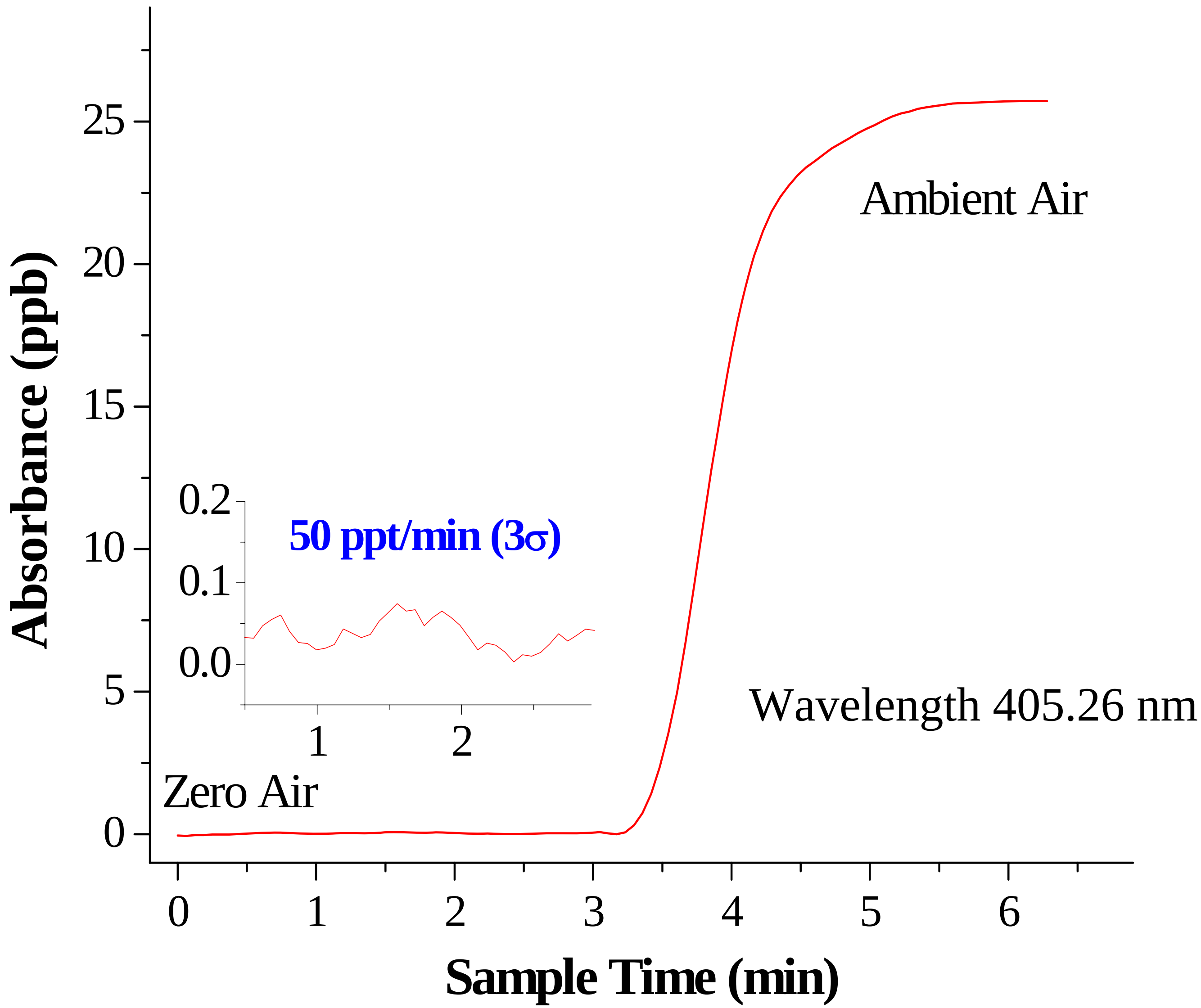


- **Detection sensitivity** **5 ppb/15 s (3σ)**
- **Recently improved to** **1 ppb/15 s (3σ)** **with high-quality mirrors (τ_0 ~ 10 μs)**
- **Ambient HONO** **0.1 ppb – 15 ppb**

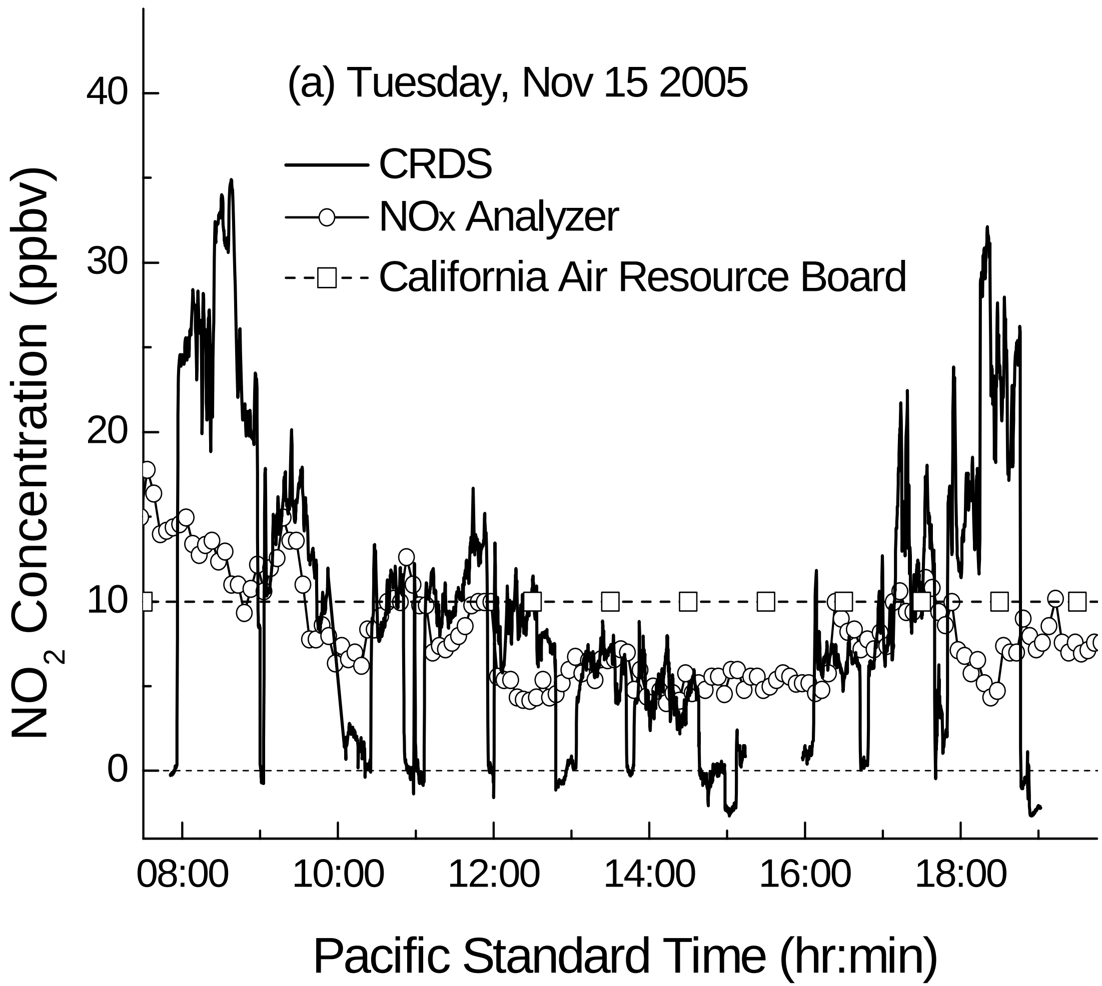
CRDS Spectrum of NO_2



CRDS Detection Sensitivity for NO_2



Variations in NO_2 concentration during daytime



Research funded by:

California Air Resources Board

U.S. Environmental Protection Agency

National Science Foundation

U.S. Department of Energy

Thank you for your attention